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Method for removing a nitrogen oxide from a gas

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METHOD FOR REMOVING A NITROGEN OXIDE FROM A GAS

The invention pertains to a method and an apparatus for removing a nitrogen oxide (NO_x) from a gas by bringing the gas in contact with a scrub liquid in a scrubber for converting the nitrogen oxide to molecular nitrogen (N₂), wherein the scrub liquid comprises a metal-ion chelate and a biomass, after which at least a portion of the scrub liquid is subjected to a membrane-separation process for separating at least part of the metal-ion chelate, and the biomass and other water-insoluble components, from water-soluble components.

A method of this type is known and is described in detail in WO 96/24434. Thus a flue gas is scrubbed with a circulating scrub liquid containing a transition-metal chelate such as iron EDTA. The complex formed from NO and transition metal chelate and/or any spent transition metal chelate is regenerated biologically, NO and NO₂ being reduced to molecular nitrogen (N₂). Contact of gaseous streams comprising NO with solutions of such metal-ion chelates, which are biologically regenerated can thus be a highly effective process for the removal and conversion of noxious NO and NO₂ into molecular nitrogen which can be discharged directly into the environment.

The Invention also relates to a method for simultaneously removing sulfur dioxide and nitrogen oxides from a gas, as was described in WO 00/02646. Thus, it is known to scrub both sulfur oxides and nitrogen oxides as gaseous components from a gas by causing the gas to rise in a scrubber, the gas being brought into contact with a scrub liquid in the form of a slurry comprising biomass, preferably comprising at least one of bacteria and yeast, transition-metal chelate, and a calcium compound suitable for binding sulfur oxides, such as lime or limestone, which rains down from spray bars in the scrubber. Whereas the nitrogen oxides (NO_x) are removed and biologically converted to molecular nitrogen as described above, sulfur oxides are removed by reacting with the calcium compound to form calcium sulfite which is oxidized further, inside or outside the scrubber, to calcium sulfate which is separated and land filled or used in construction.

Under certain operating conditions, the aforementioned processes may have severe limitations. Contaminants are introduced into the reaction solution via the gaseous stream and/or via the make-up water added to the system and degradation products

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build up as a result of oxidation of the metal-ion chelate by oxygen present in the process. Contaminants can be inorganic compounds such as hydrochloric and sulfuric acid, being scrubbed from the gas to yield chloride or sulfate salts, or organic compounds such as those resulting from the degradation of chelates or being scrubbed

5 from the gaseous stream. The contaminants that enter the process via the make-up water can be inorganic salts, such as sodium chloride, and organic compounds, such as humic acids. Inorganic compounds can build up to levels that interfere with the NO_x and SO_x absorption steps, or that inhibit biomass growth and/or metal-ion chelate regeneration activity, making the replacement of the reaction solution necessary.

10 Dilution of the metal-ion chelate content by water absorption may be troublesome, requiring addition of more metal-ion chelate, or evaporative concentration of the scrub liquid, or even the replacement of scrub liquid by fresh liquid.

15 WO 00/02646 describes a method for the removal of the chelate from the process overflow that is discharged to keep the amount of scrub liquid and contaminants at a suitable level. This involves passing that part of the overflow that is to be discharged through a chelate separator in the form of a membrane filter or some other device suitable for this purpose. No further information on the specific nature of the membrane filter was disclosed. However, specific membrane filtration processes are known in the art and effective for separation of organic molecules and monovalent ions. For instance, in J. Schaep et al., Separation and Purification Technology, 14 (1998), 155-20 162, nanofiltration membranes were used and found to have low retention for chloride ions (magnesium and sodium chloride), contrary to the much higher retentions of divalent anions. The low retention of halogenide ions enables the separation of halogenide ions from metal-ion chelates. An important problem with such membrane 25 process is encountered when the feed comprises biomass, which is necessary for the removal of NO_x, because severe membrane fouling may occur. Moreover, when SO_x is removed simultaneously with NO_x, the separation efficiency is further hampered by scaling of calcium sulfate, calcium sulfite, and/or fines derived thereof from saturated or supersaturated solutions. Thus the use of nanofiltration in separating metal-ion 30 chelates from contaminants of biomass-containing scrub liquids as used for the removal of NO_x and SO_x is practically limited or impossible due to the fouling by biomass as well as the precipitation and/or scaling of water-insoluble compounds, such as calcium carbonate, calcium sulfate, calcium sulfite, magnesium sulfate, and silica.

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Standard solutions for preventing scaling are known from, for instance, the reference works Membrane Handbook (edited by Ho and Sirkar, 1992) and Water Treatment Membrane Processes (edited by Mallevialle et al., 1996) and include the addition of auxiliary compounds such as acids, water softening agents, complexing agents or anti-scaling agents. These standard methods are often insufficient to fully prevent scaling, and more importantly, their application in scrub liquids for the removal of NO_x is disadvantageous. First, the addition of an auxiliary agent such as a softening agent further increases the purification costs, and secondly the presence of these agents can impair the removal of gaseous components from the gas or the biological transformation of NO_x in molecular nitrogen. It can also hinder the regeneration of the metal-ion chelate, which may lead to additional purification problems when the auxiliary agent must be removed.

EP 0 582 632 B1 discloses a process for the separation of metal-ion chelates from contaminants and degradation products in the presence of insoluble sulfur. The characterizing feature of this process is that the reaction solution is first fed to a microfiltration or ultrafiltration membrane to produce a fully clarified reaction solution filtrate, which is essentially free of suspended sulfur. The latter solution is then fed to a nanofiltration membrane to produce a permeate portion comprising water and solutes of up to 225 molecular weight dissolved therein, and a non-permeate concentration portion comprising water and the metal-ion chelate. Although such an approach works for the separation of sulfur particles, the method is inappropriate for the separation of biomass-comprising scrub liquid and/or (super-saturated) sulfate salts. The biomass, because of its small particulate size, would be lost in the first filtration step and both the first filtration step and the nanofiltration step would suffer from scaling due to the presence of supersaturated inorganic compounds, notably calcium sulfate and/or sulfite.

A need thus continues to exist for means to control the concentration of a metal-ion chelate in a scrub liquid that is used in a cyclic process for NO_x -removal from gaseous streams, wherein commonly accepted metal-ion chelates such as NTA, DTPA, EDTA, and/or HEDTA are employed. Furthermore, a need exists for means to control the build-up of undesirable compounds in the scrub liquid, such as chelate degradation products, inorganic salts, and low-molecular weight organic contaminants. This need is critical in applications where NO_x and SO_x are scrubbed from a gas also containing high concentrations of hydrochloric acid, such as may be the case in power plants that

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are fueled by coal having a high chloride content, in order to control the chloride level in the scrub liquid which affects the viability of the biomass. This invention offers a solution to one or more of the above problems.

- 5 To this end a method is provided for removing a nitrogen oxide (NO_x) from a gas by bringing the gas in contact with a scrub liquid in a scrubber for converting the nitrogen oxide to molecular nitrogen (N_2), wherein the scrub liquid comprises a metal-ion chelate and a biomass, after which at least a portion of the scrub liquid is subjected to a membrane-separation process for separating at least part of the metal-ion chelate, and the biomass and other water-insoluble components, from water-soluble components, characterized in that the membrane-separation process is a two-step process comprising
- 10 a) ultrafiltering at least a portion of the scrub liquid to provide a first retentate liquid comprising the biomass and other water-insoluble components, and a first permeate liquid comprising at least part of the metal-ion chelate and water-soluble components, followed by
- 15 b) nanofiltering the first permeate liquid to provide a second retentate liquid comprising the metal-ion chelate and a second permeate liquid comprising water-soluble components, followed by
- 20 c) recycling at least part of the second retentate liquid to the scrubber.

The method of the invention is very suitable for removing NO_x from gas wherein the gas further comprises at least one of a sulfur oxide (SO_x), which is converted to at least one of a water-insoluble sulfite or sulfate salt, and the scrub liquid further comprises an agent for binding with the sulfur oxide, and wherein water-insoluble sulfite and/or sulfate salts are separated from the scrub liquid. The term "water-insoluble" means that the solubility of the sulfite or sulfate salt is less than 1 g/100 ml water at 20°C, preferably less than 0.4 g/100 ml at 20°C.

25 30 Depending on the operating conditions of the NO_x or NO_x/SO_x removal, the ultrafiltration step a) may be preceded by a pre-treatment step aimed at reducing the super- or over-saturation of inorganic salts such as calcium sulfate or sulfite. Such pre-treatment steps may include any common procedure such as using a settling tank, a temperature treatment, the addition of over-saturation-decreasing additives or the

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addition of water. Also the nanofiltration step b) may be preceded by a pre-treatment step aimed at reducing the super- or over-saturation of inorganic salts in the nanofiltration second retentate liquid. Such pretreatment steps may include the addition of auxiliary components, a temperature treatment, the addition of water, and the like. In the nanofiltration step excess water is removed from the scrub liquid and at the same time a part of the soluble inorganic salts such as chlorides and sulfates and soluble organic contaminants is removed, which otherwise would impair the operations.

The invention is illustrated by the following figures.

10 Figure 1 shows a first embodiment of an apparatus suitable for purifying a gas comprising NO_x .

Figure 2 shows an embodiment of an apparatus suitable for purifying a gas comprising both NO_x and SO_x .

Figure 3 is another embodiment for purifying a gas comprising both NO_x and SO_x .

15 Figure 1 illustrates a process according to this invention in which nitrogen oxides are removed from a gaseous stream, followed by treatment and recycle of the reaction solution. Figure 1 a scrubber 1 having a gas inlet 2 for introduction of the gas to be cleaned into the scrubber 1 in the direction indicated by the arrow 3. In the bottom section 4 of scrubber 1 a recirculation tank 5 is present with the biomass in the form of free cells, which are regenerated together with the scrub liquid. A recirculation line 6 with pump 7 is connected to the bottom section 4. The recirculation line 6 is connected to at least one row of spray bars 8. Scrub liquid, which together with the biomass in circulation tank 5 is present in the bottom section 4 of the scrubber, is passed by means of the pump 7 through the recirculation line 6 into the spray bars and then falls down in the form of droplets. The dropping droplets which come in contact with gas rising in the scrubber absorb nitrogen oxides. The scrubbed gas passes the spray bars 8 and the optional demisters 9 and leaves the scrubber via discharge line 10 in the direction indicated by the arrow 11.

20 30 The scrub liquid is provided with the agents necessary for removing nitrogen oxides, such as iron chelate. For the purpose of replenishing, the scrubber is provided with a first make-up line 12 for replenishing chelate, although such a line may also be attached elsewhere in the system.

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A portion of the scrub liquid flowing through the recirculation line 6 is drawn off via a draw-off line 13 and is passed by means of pump 14 to an ultrafiltration unit (comprising the ultrafiltration membrane) 15 where suspended biomass is removed to provide a fully clarified first permeate stream. A stream enriched in biomass may be returned via line 16 to the process. The clarified stream, containing metal-ion chelate and soluble contaminants, is fed by means of a pump 17 to a nanofiltration unit (comprising the nanofiltration membrane) 18 wherein a portion of the water and low-molecular-weight, soluble contaminants are drawn off as a second permeate stream 19 to be discharged or processed further downstream. The second retentate stream from the nanofiltration unit 18 containing the metal-ion chelate may be returned into the process via line 28. The ultrafiltration unit 15 and the nanofiltration unit 18 can both be operated in different modes, such as a single pass, feed- and bleed, and the diafiltration modes. The nanofiltration unit is preferably operated in the diafiltration mode.

Figure 2 illustrates a process according to this invention in which nitrogen oxides and sulfur oxides are simultaneously removed from a gaseous stream, followed by treatment and recycle of the reaction solution. In Figure 2, elements with the same reference numerals as in Figure 1 have the same or analogous functions. The scrub liquid in scrubber 1 is provided with agents for removing both nitrogen oxides, such as a chelate, and sulfur oxides, such as limestone or other SO₂ absorbing agents. For the purpose of replenishing agents for removing sulfur oxides, the scrubber 1 is provided with a second make-up line 20.

A portion of the scrub liquid flowing through the recirculation line 6 is drawn off via a draw-off line 13 and is passed to a reactor 21. The reactor 21 is provided with a feed line 22 for supplying oxygen, preferably in the form of air, to the reactor 21. In reactor 21 the calcium sulfite from the scrub liquid is converted to calcium sulfate by the oxygen supplied. Preferably, this further oxidation is carried out outside the scrubber, to prevent or at least limit oxidation of the metal from the metal-ion chelate.

The bottom section 4 of the scrubber wherein is provided the recirculation tank 5, is not only used as a bioreactor but also as a crystallizer. Calcium sulfite and sulfate formed will, as a result of super-saturation, precipitate as crystals, which will continue to accrete over the residence time. Calcium sulfate together with scrub liquid is passed from the reactor 21 via transfer line 23, in which a pump 24 is incorporated, to a gypsum dewatering apparatus. This gypsum dewatering apparatus comprises a

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hydrocyclone 25 and a centrifuge 26. The dried gypsum from the centrifuge 26 is stored in a storage space 27. Other gypsum dewatering installations are also possible. The overflow of the hydrocyclone 25 is partially recycled, via return lines 28 and 16. Overflow to be discharged is passed via a line 29 to a pre-treatment module 30 which may consist of a settling tank, a thickener, a hydrocyclone, and/or means to perform a temperature treatment or the addition of over-saturation-decreasing additives. Alternatively, it may involve the addition of strong bases through line 31 such as calcium hydroxide or sodium hydroxide to precipitate metal hydroxides and which furnishes the chelate in the uncoordinated form to the ultrafiltration unit 15. Preferably, it consists of diluting scrub liquid with water through line 31. Whatever the nature of the treatment, the pre-treatment module 30 furnishes a scrub liquid, which is no longer super-saturated in calcium sulfate and/or sulfite, to ultrafiltration unit 15. In the pre-treatment step monovalent cations, such as sodium or potassium ions, may be added to the feed solution to further improve the separation, in particular to lower the chloride retention in the nanofiltration step. Pump 14 provides the no longer super-saturated scrub liquid to an ultrafiltration membrane in unit 15 where suspended biomass and remaining inorganic insoluble salts are removed to provide a clarified first permeate liquid stream. A stream enriched in biomass may be returned via line 16 into the process. The clarified stream, containing metal-ion chelate and soluble contaminants, is fed by means of a pump 17 to a nanofiltration membrane in unit 18 wherein a portion of the water and low-molecular-weight, soluble contaminants are drawn off as a second permeate stream 19 to be discharged or processed further downstream. The second retentate stream from the nanofiltration unit is returned to the process via line 28. The overflow of an installation designed for the removal of SO_x that is not equipped with the membranes according to the invention as described above, is usually subjected to a water treatment involving the addition of an alkaline reagent such as sodium hydroxide or calcium hydroxide before it is discharged into the environment in order to remove heavy metals and other ingredients that are scrubbed from the flue gases. The resulting precipitate is removed from the aqueous phase in a clarifier, so that the final aqueous stream can be directly discharged. Under certain process conditions it is possible to optimize the total process by modifying the relative positions and functions of the membrane-filtration step and the water-treatment unit. Useful ways to do so include a) the placement of the membrane filtration step after the water-treatment step, b) the complete substitution of the water-treatment step by the

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membrane filtration step, or c) passing a part of the overflow through the membrane-filtration units and a part through the water-treatment units, and combining both streams in such a way that the total stream conforms to discharge requirements.

In Figure 3 elements with the same reference numerals as in Figure 1 have the same or analogous functions. In Figure 3 a sodium-containing compound, preferably aqueous sodium hydroxide, is added to the scrub liquid via a make-up line 20. A portion of the scrub liquid which is recirculated through line 6 and which contains sodium sulfite, sodium sulfate, and chelate is passed, via draw-off line 13, to the ultrafiltration unit 15 and via pump 17 to the nanofiltration unit 18. The biomass- and chelate-containing portion of the scrub liquid is recycled to the scrubber 1 via lines 16,28. The sodium sulfite- and sodium sulfate-containing portion of the scrub-liquid drawn off is passed to a reactor 21 via line 32. Reactor 21 is supplied with oxygen via line 22, which converts the sodium sulfite into sodium sulfate. Sodium sulfate-containing and scrub liquid-containing fluid is discharged via discharge line 19.

This invention is not limited by the embodiments illustrated and the skilled artisan will recognize that multiple variations of the process illustrated are possible. Such variations include the removal of pre-treatment module 30.

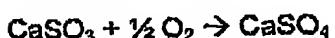
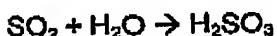
NO_x and/or SO_x are contained in various gaseous streams. Sources include, for example oil- and coal-fueled power plants, pelletizing plants, catalyst production units, nitric acid plants, and non-ferrous metal smelters. NO_x and SO_x are toxic gases adding to the greenhouse effect and acid rain. Contact of a gaseous stream containing NO_x with an aqueous absorption solution is very effective in the removal of NO_x, if the aqueous absorption solution contains a metal ion capable of binding NO, the component in NO_x which is least soluble in water, as well as a biomass capable of transforming water-solubilized nitrogen oxides in molecular nitrogen. A chemical reaction takes place between the metal ion and NO, whereby NO is bound to the water-soluble metal ion.

Suitable metal ions for the binding of NO are ions derived from iron, manganese, and ruthenium. Particularly preferred are ions derived from iron, the higher (i.e. oxidized) valence state being ferric ion and the lower (i.e. reduced) valence state being ferrous ion, the lower state being able to bind NO. Operable concentrations of the metal ion in the scrub liquid will range from several micromoles to 0.5 M. Preferable concentrations will range from 10 to 100 mM.

The metal ion is preferably employed in a water-based solution as a soluble coordination compound in which the metal ion is bound to a chelate. A chelate may be defined as a molecule that contains two or more coordinating groups capable of associating with a metal ion to form a coordination compound. The coordination compound that results from the binding of the metal ions by the chelate or chelates may be referred to as a metal-ion chelate. Preferred chelates are organic polycarboxylic acids such as citric acid or aminopolycarboxylic acids. Particularly preferred are aminopolycarboxylic acids derived from ammonia, ethylenediamine, propylenediamine, diethylenetriamine, or 2-hydroxyalkyl amines. Examples of such chelates which may be advantageously used include nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), N-hydroxylethylethylenediamine-N,N',N"-triacetic acid (HEDTA), diethylenetriamine-N,N,N',N",N"-pentaacetic acid (DTPA), nitrilotripropionic acid, and ethylenediaminetetrapropionic acid. These may be employed as the acids or their salts, particularly their ammonium or alkali salts. Mixtures of these acids or their salts may be used. Mixtures of the aminopolycarboxylic acid chelates with other chelates such as citric acid or its salts may also be used. As used herein, the chelate also includes mixtures of chelate compounds. Especially preferred polyvalent metal ion chelates are the ferrous ion chelates formed from NTA, EDTA or HEDTA, most preferably ferrous EDTA.

Operable concentrations of chelant may range widely, but are preferably equimolar with the oxidizing polyvalent metal ion. An excess or a deficiency of the chelate may advantageously be employed, e.g., 10 to 40 mole percent excess or deficiency, relative to the metal ion.

Contact of a gaseous stream comprising SO_x with an aqueous absorption solution is also very effective in the removal of SO_x, if the aqueous absorption solution contains a calcium compound such as calcium hydroxide and calcium carbonate that will react with the SO_x present in the gas, particularly sulfur dioxide, to produce sulfurous acid in the scrub liquid. The sulfurous acid is converted to calcium sulfite, which in the presence of oxygen, will oxidize further to calcium sulfate according to the following reactions (for calcium carbonate being the calcium compound):



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For NO_x or NO_x and SO_x removal, the aqueous absorption solution containing the metal-ion chelate and biomass and/or the calcium compound is brought into contact with the gaseous stream in a gas-liquid contactor. The preferred choice of gas-liquid contactor type will depend upon performance requirements for each use. During

5 gas-liquid contact with a gaseous stream NO₂ will be absorbed by the scrub liquid, whereas the water-soluble metal-ion chelate will react with NO to produce a water-soluble metal-ion-NO chelate complex. The metal-ion chelate is regenerated biologically by the biomass. In the presence of a calcium compound also sulfur oxides are scrubbed from the gas stream to produce calcium sulfite and/or calcium sulfate.

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The scrub liquid comprising the metal ion chelate and the biomass and optionally the insoluble and soluble inorganic salts, is separated from the treated gas stream and is drawn into a loop for treatment and recycle. If the scrub liquid is provided with agents for removing SO_x, most or all of the scrub liquid is treated to remove suspended

15 calcium sulfate and/or calcium sulfite. This may comprise passing the scrub liquid through a hydrocyclone or, more simply, a thickening vessel such as a settling tank. Filterability of the calcium sulfite/calcium sulfate dispersion will vary depending upon process conditions. The calcium sulfate and/or calcium sulfite removed as a filter cake by the treatment unit may be sent on for further dewatering and/or processing.

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In any calcium sulfite/calcium sulfate dispersion obtained through the scrubbing of SO_x, some particulate calcium sulfate/sulfite will be incompletely removed by this treatment and will be present in the overflow.

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The SO_x react with calcium salts in the aqueous phase to produce calcium sulfite, which may be partially converted to calcium sulfate, due to the presence of oxygen in the feed gas. It may however be necessary or desirable to oxidize also the remaining calcium sulfite into calcium sulfate in the presence of extra oxygen or air. This is preferably done in a separate reaction vessel and not in the scrubber. If calcium sulfite were to be oxidized in the scrubber the metal-ion chelate would consistently be subject to high concentrations of oxygen leading to the inactive oxidized metal-ion chelate necessitating a higher activity, thus increased cost, of the biological regeneration.

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A portion of the scrub liquid is drawn off from the process treatment loop and passed through a secondary process treatment loop involving an ultrafiltration unit and a nanofiltration membrane unit. The ultrafiltration step may be, but is not necessarily, preceded by a treatment aimed at reducing the super- or over-saturation of inorganic

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salts such as calcium sulfate or sulfite in the ultrafiltration feed stream. Also the nanofiltration step may be, but is not necessarily, preceded by a treatment aimed at removing the super- or over-saturation of inorganic salts in the nanofiltration second retentate stream. This may involve temperature treatment, the addition of auxiliary components or the addition of fresh water, i.e. water not saturated in the inorganic salts causing the super- or over-saturation (for instance of calcium sulfate or calcium sulfite). The ultrafiltration unit is chosen on the basis of its ability to provide a fully clarified filtrate essentially free of suspended biomass and optionally free of calcium sulfite/sulfate fines, to the nanofiltration unit. This ultrafiltration unit may consist of any of several basic porous membrane types made of polysulfone, polyethersulfone, polyvinylidfluoride, polyacrylonitrile, or modified versions such as e.g. hydrophilized polysulfone. The molecular weight cut-off of the membranes are in the range of 1000 Dalton to 1,000,000 Dalton, preferably in the range of 10,000 to 100,000 Dalton, and more preferably in the range of 20,000 to 50,000 Dalton, so long as it meets the basic requirement of providing a biomass-free and fines-free filtrate. The ultrafiltration module can be in the form of a tubular module, a capillary module, a plate-and-frame or a (vibrated) disc-module. Preferably, the tubular module or the capillary module is used. The filtrate from the ultrafiltration step is to be fully clarified, that is, essentially free of all suspended biomass and fines. A fully clarified reaction solution is defined in this case to be a solution with turbidity (NTU) smaller than 50, preferably below 10 and more preferably below 1. The fully clarified reaction solution is to be otherwise optimally about the same as the feed solution to the second filtration unit in respect to content of dissolved inorganic salts and low-molecular-weight organic solutes of up to 1,000,000 Dalton, depending on the molecular weight cut-off of the ultrafiltration membrane. All or a portion of this essentially biomass- and fine-free pass liquid is fed to a membrane device containing a nanofiltration membrane effective for removal of water, inorganic salts and low molecular organic solutes from the clarified metal ion chelate solution. Low-molecular weight is defined in this context to be between 150 and 300 g/mol molecular weight and less. Suitable nanofiltration membrane devices may consist of asymmetric phase inversion membranes or thin film composite membranes. Examples of membranes meeting these requirements are disclosed in US-A-4,247,401 and US-A-4,834,886. US-A-4,247,401 describes porous asymmetric membranes formed from acetylated cellulose modified with covalently bonded dyestuffs. US-A-4,834,886 describes thin film composite membranes in which the active permselective layer is a

crosslinked polyvinyl alcohol. Membrane compositions other than these are also possible: e.g. acetylated cellulose, polyamide, polysulfone, polyethersulfone, sulfonated polyethersulfone, poly(piperazine, poly(piperazineamide, poly(piperazine-polyamide and aromatic polyamide. Particularly advantageous are sulfonated polyethersulfone membranes or poly(piperazineamide membranes. The nanofiltration module can be in the form of a tubular module, a capillary module, a plate-and-frame, a (vibrated) disc-module or a spiral wound module. Preferably the spiral wound module is used and are ideally suited to treatment of feed solutions that have been fully clarified in a preceding filtration step. The nanofiltration membrane device may be operated at hydraulic pressures on the feed side over a wide range, provided the membrane will tolerate the transmembrane pressure. A pressure in the range of 0.35 to 10 Mpa (50 to 1500 psig) is generally advantageous, preferably 0.7 to 7 Mpa (100 to 1000 psig), more preferably 1.4 to 5.5 Mpa (200 to 800 psig). Actual selection of a hydraulic feed pressure will depend upon several factors, including membrane type, the total solute concentration of the reaction solution being provided as feed to the device, the reaction solution temperature, the membrane permeation rate, and the pressure limitations of the membrane device. The required hydraulic pressure is conveniently provided by means of a pressurizing pump, the selection of which is readily made by the skilled person.

The temperature of the feed solution to the membrane device may vary from 0 to 95°C, provided the membrane and associated components are not deleteriously affected. However, the feed temperature is preferably controlled to values between 20 and 50°C. Each salt, such as calcium sulfate and calcium sulfite, has a critical temperature above which the process temperature should preferably not increase during the separation process, in order to avoid the occurrence of super-saturation of calcium sulfate and/or sulfite, which would cause deleterious scaling of the membrane. For calcium sulfate the process temperature should not increase during the separation process when the temperature is about 36°C or higher.

The nanofiltration membrane device receives the fully clarified metal-ion chelate solution and operationally converts it into two exit streams: a concentrate stream selectively enriched in the metal-ion chelate, and a permeate stream depleted in the metal-ion chelate and containing most of the contaminants. The concentrate stream enriched in metal-ion chelate is recycled to the primary process loop. The permeate is either discarded from the process or treated further. Further treatment may include

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recycle through a second stage nanofiltration membrane device for additional recovery of metal ion chelate moieties that may have permeated through the initial nanofiltration membrane device. Preferably, a nanofiltration membrane is selected for the initial nanofiltration treatment step that eliminates the need for such additional treatment of the second permeate from this initial nanofiltration step. The nanofiltration membrane should be capable of permeating water, inorganic salts dissolved therein, and low-molecular-weight organic compounds of up to 150 to 300 molecular weight dissolved therein, while effectively concentrating metal ion chelate moieties of 150 to 300 molecular weight or higher.

The metal-ion chelate in the process liquids can be in the form a metal-chelate coordination compound, such as iron EDTA, or equally in the form of the metal-ion chelate not bound to the metal ion.

The method of the invention has the advantage that it is able to remove biomass from scrub liquid and to control the concentration of metal-ion chelate together with that of contaminants that can impair the operations, that it effectively prevents scaling due to the occurrence of over-saturated solutions of calcium sulfite and/or sulfate and that it does not require addition of auxillary components.

The method of the invention is useful when the discharge of metal-ion chelate, in order to control the concentration of contaminants would negatively affect the cost-performance of the process. The method of the invention is particularly useful when the discharge of metal-ion chelate is prevented from an environmental point of view. The method is further very suitable for the separation of chelating agents, preferably an amino polycarboxylic acid such as EDTA, from inorganic salts.

The following examples are presented to illustrate this invention, but are not intended to limit the scope of the invention.

Example 1

A recycle solution from a process for the removal of NO_x comprised biomass, sodium ions, sulfate ions, chloride ions, and Fe-EDTA. This solution was fed to a hollow fiber polysulfone ultrafiltration module from KOCH with a MWCO of 500,000 Dalton. At a pressure of 3 bar and at room temperature, 80% of the feed was successfully cleaned from biomass and fines. The clear permeate solutions were transferred to the nanofiltration unit and the concentrate solution was recycled to the scrubber system.

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Example 2

A recycle solution from a process for the removal of NO_x comprised biomass, sodium ions, sulfate ions, chloride ions, and Fe-EDTA. The solution was fed to a tubular modified polysulfone ultrafiltration module from Stork with a MWCO of 50,000 Dalton.

- 5 At a pressure of 4 bar and at room temperature, 90% of the feed was successfully cleaned from biomass and fines. The clear permeate was subsequently treated with a spiral wound sulfonated polyethersulfone nanofiltration membrane. At a pressure of 20 bar and at room temperature the Fe-EDTA was successfully separated from the inorganic salts: the Fe-EDTA, sulfate and chloride retentions were respectively 82%,
10 24% and -7%. The concentrate solution, containing most of the Fe-EDTA solute, was recycled to the scrubber process, whereas the salt containing permeate flow, with a strongly reduced Fe-EDTA concentration, was discharged.

Example 3

- 15 A recycle solution from a process for the combined removal of SO_x and NO_x comprised suspended solids (calcium sulfite and calcium sulfate), biomass, dissolved sodium, potassium, calcium and magnesium ions, dissolved chloride and sulfate ions, and Fe-EDTA. The solution was fed to a tubular modified polysulfone ultrafiltration module from Stork with a MWCO of 50,000 Dalton. At a pressure of 3 bar and at room temperature
20 the feed was successfully cleaned from biomass and suspended solids. NTU's smaller than 10 were obtained. The clear permeate was subsequently treated with a spiral wound poly(piperazineamide) nanofiltration membrane. At a pressure of 10 bar and at room temperature the Fe-EDTA was successfully separated from the inorganic monovalent salts: the Fe-EDTA retentions were in the range of 99.0 to 99.8%. The chloride retentions were in the range of -5 to 40% depending on the composition of the solution. The concentrate solution containing all of the Fe-EDTA was recycled to the process, whereas the monovalent salt containing permeate flow, with almost no Fe-EDTA, was discharged.
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Claims

1. A method for removing a nitrogen oxide (NO_x) from a gas by bringing the gas in contact with a scrub liquid in a scrubber for converting the nitrogen oxide to molecular nitrogen (N_2), wherein the scrub liquid comprises a metal-ion chelate and a biomass, after which at least a portion of the scrub liquid is subjected to a membrane-separation process for separating at least part of the metal-ion chelate, and the biomass and other water-insoluble components, from water-soluble components, characterized in that the membrane-separation process is a two-step process comprising
 - 5 a) ultrafiltering at least a portion of the scrub liquid to provide a first retentate liquid comprising the biomass and other water-insoluble components, and a first permeate liquid comprising at least part of the metal-ion chelate and water-soluble components, followed by
 - 10 b) nanofiltering the first permeate liquid to give a second retentate liquid comprising the metal-ion chelate and a second permeate liquid comprising water-soluble components, followed by
 - 15 c) recycling at least part of the second retentate liquid to the scrubber.
2. The method according to claim 1 wherein the gas further comprises at least one of a sulfur oxide (SO_x), which is converted to at least one of a water-insoluble sulfite or sulfate salt, and the scrub liquid further comprises an agent for binding with the sulfur oxide, and wherein water-insoluble sulfite and/or sulfate salts are separated from the scrub liquid.
- 20 3. The method according to claim 1 or 2 wherein the gas further comprises heavy metals.
4. The method according to any one of claims 1-3 wherein the conversion of the nitrogen oxide to molecular nitrogen is brought about by the biomass.
- 25 5. The method according to any one of claims 1-4 wherein the agent for binding with the sulfur oxide comprises at least one of calcium and magnesium ions.
- 30 6. The method according to any one of claims 1-5 wherein the water-soluble components of the permeate liquid comprise at least one of chloride and sulfate ions.

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7. The method according to any one of claims 1-6 wherein the biomass comprises at least one of bacteria and yeast.

5 8. The method according to any one of claims 1-7 wherein the metal-ion chelate comprises an amino polycarboxylic acid, preferably ethylenediaminetetraacetic acid (EDTA) and a transition metal-ion, preferably a ferrous ion.

10 9. The method according to any one of claims 1-8 wherein the ultrafiltration membrane is selected from polysulfone, polyethersulfone, polyvinylidifluoride, polyacrylonitrile, or modified versions thereof, and the nanofiltration membrane is selected from asymmetric phase inversion membranes or thin film composite membranes.

15 10. The method according to any one of claims 1-9 wherein monovalent cations are added to the scrub liquid.

15 11. An apparatus for performing the method of any one of claims 1-10 comprising a scrubber (1) and a membrane separation unit (15,18) characterized in that the membrane separation unit (15,18) comprises a first ultrafiltration compartment (15) and a second nanofiltration compartment (18), means (28) for transporting the retentate liquid obtained in the second nanofiltration compartment (18) to the scrubber (1) and/or means (16) for transporting the retentate liquid obtained in the first ultrafiltration compartment (15) to the scrubber (1).

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Abstract

The invention pertains to a method and an apparatus for removing a nitrogen oxide (NO_x) from a gas by bringing the gas in contact with a scrub liquid in a scrubber for converting the nitrogen oxide to molecular nitrogen (N₂), wherein the scrub liquid comprises a metal-ion chelate and a biomass, after which at least a portion of the scrub liquid is subjected to a membrane-separation process for separating at least part of the metal-ion chelate, and the biomass and other water-insoluble components, from water-soluble components, characterized in that the membrane-separation process is a two-step process comprising

- a) ultrafiltering at least a portion of the scrub liquid to provide a first retentate liquid comprising the biomass and other water-insoluble components, and a first permeate liquid comprising at least part of the metal-ion chelate and water-soluble components, followed by
- b) nanofiltering the first permeate liquid to give a second retentate liquid comprising the metal-ion chelate and a second permeate liquid comprising water-soluble components.
- c) recycling at least a portion of the second retentate liquid to the scrubber.

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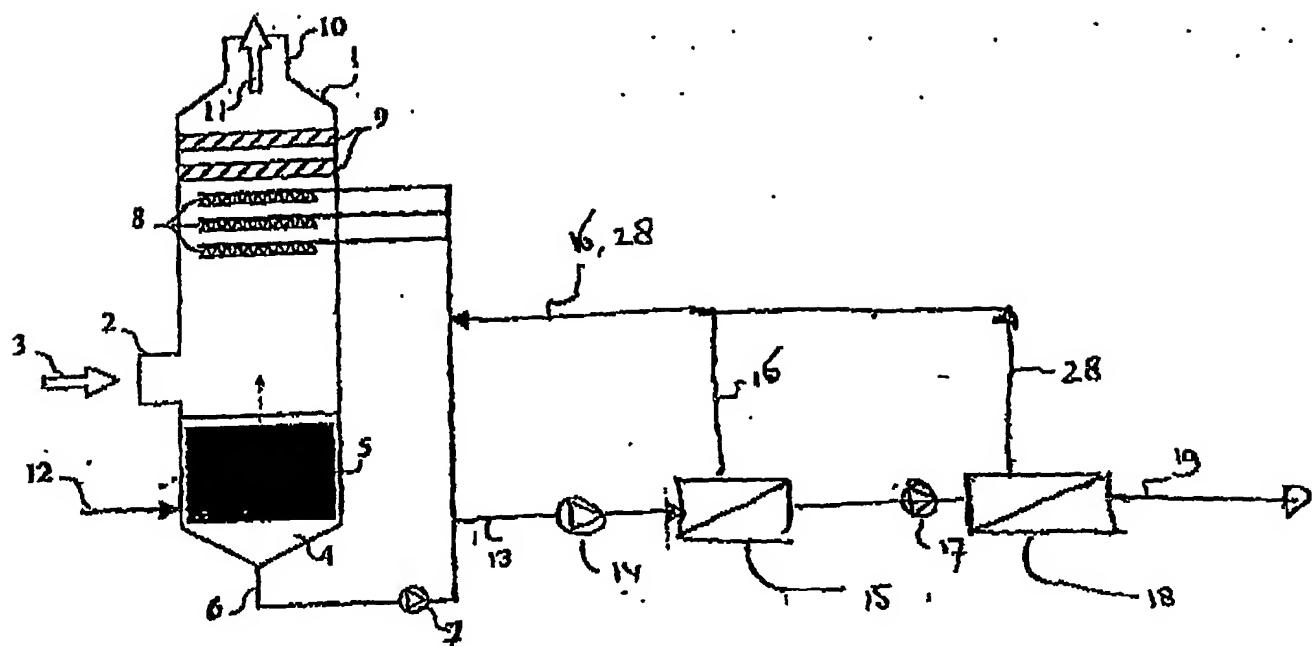


Fig. 1

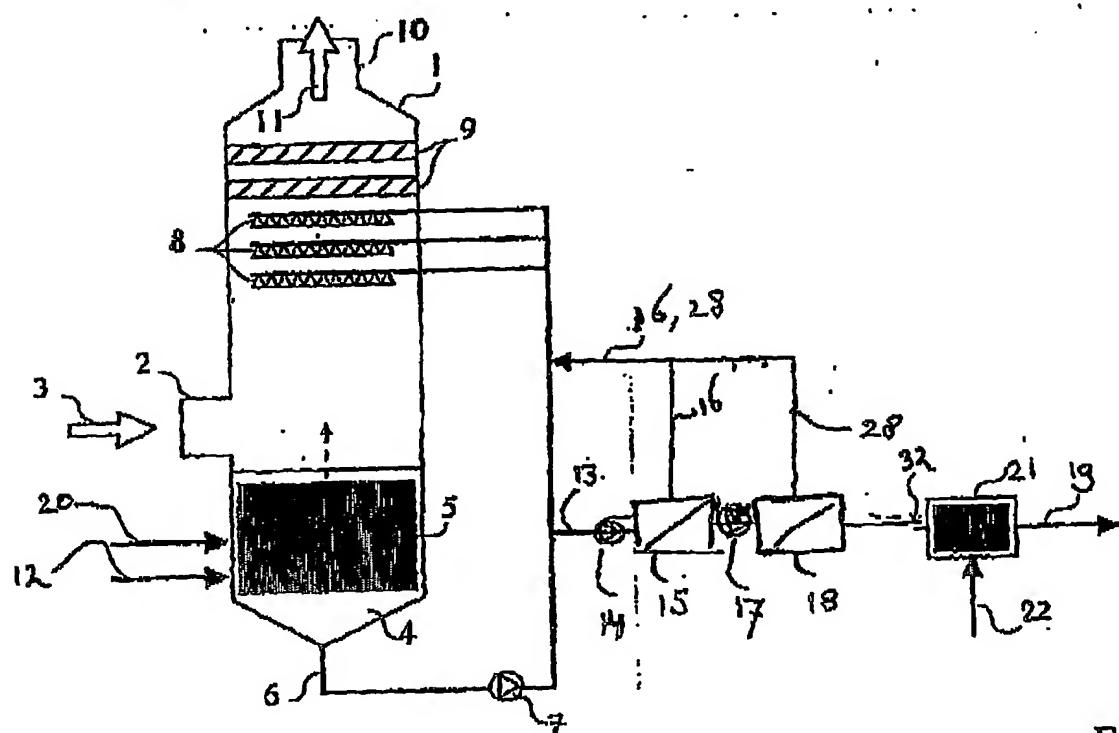


Fig. 3

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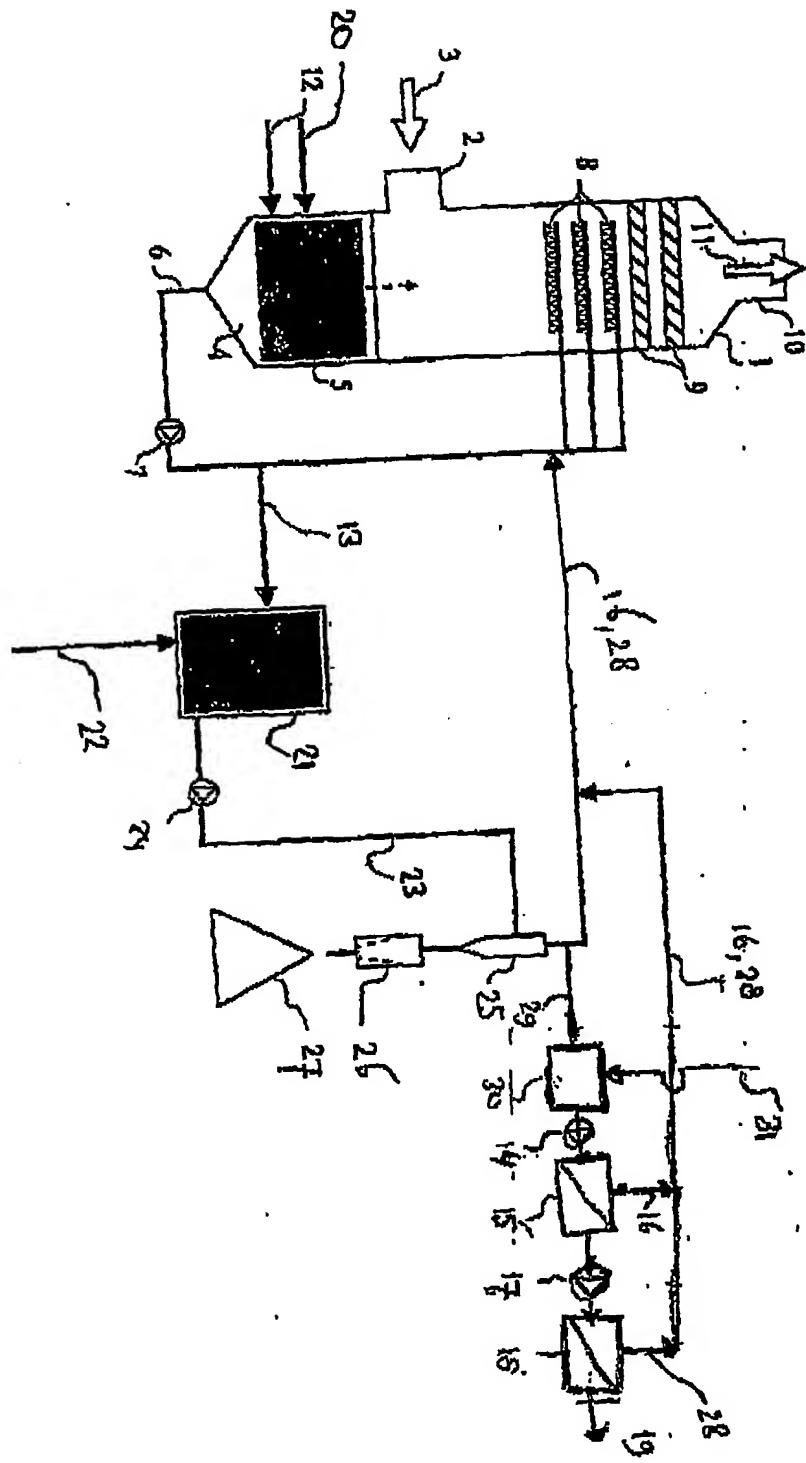


Fig. 2